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MRL-TN-440

AN ASPECT OF THE INTERNAL CORROSION OF DEFA CASES

Peter J. Knuckey and Jeffrey J. Batten

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ABSTRACT

The internal corrosion of zinc-plated steel DEFA cases was due to reaction between the zinc coating and internally derived nitric and formic acids in the vapour phase. These gave the corrosion products basic zinc nitrate and zinc formate. The predominance of formate in the outermost layers of the corrosion product and of nitrate in the lower layers suggests that corrosion processes changed at one stage. This was presumably associated with changes in the relative amounts of the two corrodents with time.

These observations are in conformity with the products formed during the thermal decomposition of nitrocellulose. These products include nitrogen dioxide, water, and formaldehyde, where nitrogen dioxide is observed in the early stages of the reaction but disappears as the reaction proceeds. Formaldehyde, on the other hand, appears to build-up to a steady concentration. The corrodent nitric acid is explained by the presence of the products nitrogen dioxide and water, while formic acid could arise from the oxidation of formaldehyde by nitrogen dioxide.

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16. ABSTRACT (if this is security classified, the announcement of this report will be similarly classified):

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These observations are in conformity with the products formed during the thermal decomposition of nitrocellulose. These products include nitrogen dioxide, water, and formaldehyde, where nitrogen dioxide is observed in the early stages of the reaction but disappears as the reaction proceeds. Formaldehyde, on the other hand, appears to build-up to a steady concentration. The corrodent nitric acid is explained by the presence of the products nitrogen dioxide and water, while formic acid could arise from the oxidation of formaldehyde by nitrogen dioxide.

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AN ASPECT OF THE INTERNAL CORROSION OF DEFA CASES

1. INTRODUCTION

The purpose of this technical note is to present the work performed during an investigation conducted on behalf of the RAAF on the cause of extensive internal corrosion in cartridge cases of French manufactured DEFA 30 mm HE ammunition. This corrosion problem was identified by the RAAF and, as this situation was of critical concern to them, they requested an investigation to assess the degree of hazard represented by the ammunition.

A white corrosion product was found on the internal surfaces of the cases during routine breakdown in a range of different ammunition lots which had been stored for various periods at a number of locations, i.e., the problem was seen to be general to this type of store. Also, while external corrosion was noted on a number of rounds due to the lives of the silica gel drying bags having become expended, no correlation between the incidence of internal and external corrosion was observed.

The propellant used in these rounds was nitrocellulose, stabilised with diphenylamine and coated with ethyl centralite and graphite. Details of rounds submitted for examination are given in Table 1. These rounds were broken down by Explosives Devices Group (MRL) prior to laboratory examination by Electrochemistry Group (MRL).

2. NATURE OF THE CORROSION PRODUCTS

2.1 General Description

The cases were a heat treated steel, and had been zinc plated and chromate passivated. No significant corrosion was observed on the external surfaces of the cases. Several had minor blooms of white corrosion product or very mildly rusted areas at points of mechanical damage to the zinc coating (mainly on the projectile crimps). However in view of the observation by RAAF on the possibility that some degree of dampness may have been encountered by the above cases during storage, the samples supplied were probably not typical of the general external condition of all stored cases. Minor corrosion was observed in the detonator holes. This gave the

impression of being due to the effect of liquid residues from the metal finishing processes, but there was no reason to think it was related to the internal corrosion problem.

The samples submitted were intended to typify the internal condition of rounds. Examination of the sectioned cases at low magnifications showed that definite corrosion of the zinc plating had occurred, although it was not heavy in any round. There was no evidence in any round of base metal (steel) corrosion.

Two main corrosion patterns were observed in the zinc coating :

- (a) A general light background of corrosion, with well defined white crystalline corrosion products, plus random individual pustules of corrosion product. Each pustule had a centrally located black mark on its upper surface (see Figures 1 and 2).
- (b) A pattern of well defined images of propellant grains, the image areas generally being free from corrosion. A general light white corrosion product was present in those areas not in direct contact with the propellant grains, i.e., on the metal surfaces in the spaces between the grains that had been exposed to vapour (see Figure 3).

2.2 Examination of Internal Corrosion Products

2.2.1 Preliminary Chemical Tests

In view of the possibility of high humidity storage conditions, as suggested by the RAAF observations, any attack by moisture on the internal surfaces of the cases would be expected to lead to zinc hydroxide and/or basic zinc carbonate corrosion products. The former is difficult to identify by chemical means. The basic carbonate would be expected to evolve carbon dioxide on acidification and, as the corrosion product did not, it was concluded that no carbonate was present. It was likely, therefore, that the external environment was not responsible for the internal corrosion and that the corrodent originated internally.

In view of the nature of the propellant (nitrocellulose) and the recognised evolution of nitrogen dioxide from this material [1,2], the corrosion products were examined for nitrate. The chemical spot test using α -naphthylamine, sulphanilic acid and zinc metal [3] positively detects nitrate in small quantity, with no interference from other materials (except nitrite, which is closely related to nitrate and is also derived from nitrogen dioxide).

Preliminary tests showed that propellant grains did not react with the reagent. However, corrosion products from all submitted rounds showed a positive nitrate reaction. The variable intensity of spot-test reaction suggested a variation in the concentration of nitrate in the samples examined, i.e., that the corrosion product was frequently not all nitrate. Even the assumption that the corrosion product was more likely to be a basic salt rather than normal zinc nitrate would not explain the observed results.

As a consequence of the instrumental analysis results reported in Section 2.2.2, semi-quantitative nitrate estimations were carried out on samples from all cases with the emphasis on detection of variation in nitrate content. Estimations were made colorimetrically, using the α -naphthylamine/sulphanilic acid reagent, by comparison with standard nitrate solutions.

Preliminary examinations showed that nitrate content varied from 10% to 100%, calculated as a basic zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot \text{Zn}(\text{OH})_2$), depending on the position of sampling. Samples taken adjacent to the metal surface were in the range 50-100%, while samples taken from the tops of the corrosion pustules were around 10-25% nitrate.

A more systematic examination of all cases was made, samples again being taken from the outer (top) layers (especially from pustule tops), and adjacent to the metal surface (lower). In all, about 100 samples were examined for nitrate content. While individual variations occurred due to sampling difficulties, the general pattern established was that of nitrate levels significantly higher at the metal interface compared with areas further out, e.g., the pustule tops. The results of these tests are presented in Table 2.

2.2.2 Instrumental Analyses

It should be noted that the three instrumental analysis methods used to identify the major constituents of the corrosion products identify different species. The electron probe microanalysis (EPMA) method identifies and estimates elements only. The infrared absorption (I.R.) method identifies anions (e.g., nitrate, hydroxide, etc.) and under favourable circumstances may also identify compounds. The X-ray diffraction (X-R.D.) technique identifies crystalline compounds (e.g., zinc nitrate).

The results of these analyses are as follows :

(a) EPMA

An EPMA scan was carried out over an area containing a corrosion pustule. The white corrosion product was shown to contain zinc as a major element (about 30%), while carbon and oxygen were also present in significant amounts. Unfortunately nitrogen could not be detected, as its expected concentration level (2-4%) in the corrosion product was below the sensitivity limit of the EPMA technique. For this reason also, a scan across a sectioned pustule for detection of any variation of nitrogen (i.e., nitrate) concentration was unsuccessful. The black spot at the top of the pustule was shown to be carbon and was most likely graphite derived from pressure contact with the propellant coating.

(b) X-R.D.

The initial sample examined (corresponding with a "top" sample in the chemical tests) was identified as zinc formate dihydrate. No nitrate was detected. At this time in the investigation the above result could not be explained. As a check, an independent chemical spot test confirmed the presence of formate. Several samples were prepared artificially from zinc

and formic acid. These gave identical patterns to the corrosion product, confirming its identity as zinc formate.

A second sample (corresponding with "lower", and showing high nitrate in the chemical tests) completely matched the data for a particular basic zinc nitrate, $\text{Zn}(\text{NO}_3)_2 \cdot 4 \text{Zn}(\text{OH})_2 \cdot 2 \text{H}_2\text{O}$. These results identify the corrosion product as a mixture, with a predominance of zinc formate or zinc nitrate depending on sample location.

(c) I.R.

Concurrent with the above examinations, I.R. examination of a mixed corrosion product sample showed the presence of zinc nitrate (probably basic, hydrated), and zinc formate. Because of the coincidence of the two major I.R. absorption bands for these two materials, the relative quantities could not be accurately determined. Nevertheless these results confirm the other instrumental analysis findings that the corrosion product was a mixture of zinc formate and basic zinc nitrate.

3. CASE CRACKING

During examination of the external surfaces of the corroded cases it was noted that circumferential cracking frequently occurred around the crimp used to secure the projectile. In view of the possible re-use of these cases, metallographic examinations were made of sections through the affected areas.

It was clear (see Figure 4) that the cracking observed occurred only in the zinc electroplate and did not extend into the steel substrate. It was concluded therefore that the cases had not been damaged by extraction of the HE projectiles and could safely be re-crimped if required.

4. DISCUSSION

(a) The formation of a basic zinc nitrate probably occurs in two stages:

- (i) initial formation of zinc nitrate, stable in acidic conditions and,
- (ii) slow hydrolysis, as a second stage, to form the basic salt.

The second stage (ii) would only occur in very low acid or near-neutral conditions as the basic salt would be unstable in acidic conditions. General experience at MRL has been that such changes frequently occur in corrosion products and proceed very slowly.

This implies that the formation of nitrogen dioxide diminishes with time from some initial peak value to a very low or even zero rate over an extended time period, and also that formic acid was not present in appreciable concentration during this time.

(b) It is likely that formic acid vapour would react readily with any preformed basic groups of the basic zinc nitrate to form zinc formate. This mechanism would explain the non-uniform distribution of formate, which has been shown to be generally in higher concentration in the outer regions of the corrosion product layers.

5. CONCLUSIONS

- (a) Mild corrosion was observed internally in all of the 18 cases examined, and externally on some cases. The external corrosion is considered to be trivial in the present context and is not discussed further. In no instance was the base metal (steel) corroded internally and in no instance was the structural strength of the case adversely affected.
- (b) Internal corrosion was clearly due to reaction between the zinc coating and internally-derived corrosives in the vapour phase.
- (c) The corrosion products were positively identified as zinc formate and a basic zinc nitrate, indicating that the corrosives were formic and nitric acids.
- (d) The various analysis methods available gave a good consensus as to the composition of the corrosion products.
- (e) The predominance of formate in the outermost layers of the corrosion product and of nitrate in the lower layers suggests that the corrosion processes changed at one stage. This was presumably associated with changes in the relative amounts of the two corrosives with time.
- (f) The presence of nitric acid can be explained by the formation of nitrogen dioxide and water during the normal spontaneous, but slow, degradation of the nitrocellulose propellant [1,2].
- (g) The composition of the corrosion product indicates that formic acid was a major end product of the degradation of nitrocellulose, presumably being derived from the little recognised degradation product, formaldehyde. For example, such notable texts on explosives as [1] and [2] do not mention formaldehyde as one of the major degradation products from nitrocellulose.
- (h) In agreement with (e) above, nitrogen dioxide is observed in the early stages of the degradation reaction but disappears as the reaction proceeds. Formaldehyde, on the other hand, appears to build-up to a steady concentration.
- (i) Aspects of this work relating to the mechanism of degradation of nitrocellulose, and the formation and subsequent reactions of its major degradation products (nitrogen dioxide and formaldehyde), will be discussed in a separate publication.

6. ACKNOWLEDGEMENTS

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T A B L E 1

DETAILS OF ROUNDS SUBMITTED TO ELECTROCHEMISTRY
GROUP, MRL, FOR EXAMINATION

Case No. (MRL Designation)	Round Markings	Storage Location
1,2,3	Lot 4 MR 65/0 17 TE 64 6 MR 65 CS	Tropical, 8 years
4,6,9	Lot 7 MR 66/0 17 TE 65 10 MR 66 CS	Tropical, 5 years then 1 CAMD, 2 years
5,7	Lot 10 MR 67/0 20 TE 65 16 MR 67 CS	1 CAMD
8	Lot 10 MR 67/0 20 TE 65 10 MR 65 CS	1 CAMD
10,11,13	Lot 1 MR 71/0 15 TE 69 22 MR 70 CS	Tropical, 6 years
12,14,16	Lot 7 MR 65/0 17 TE 64 10 MR 65 CS	Tropical, 8 years
15,17,18	Lot 1 MR 66/0 5 TE 65 15 MR 65 CS	Tropical, 6 years

TABLE 2

DISTRIBUTION OF NITRATE IN THE CORROSION PRODUCT

Lot No.	Corrosion product form	Nitrate level
Lot 4 MR 65/0	non-pustular	10 to 100%
Lot 7 MR 65/0	non-pustular	lower: 10-25% top : 50-100%
Lot 1 MR 66/0	pustular	lower: 50-100% top : 10-50%
Lot 7 MR 66/0	non-pustular	lower: 25-50% top : 10-25%
Lot 10 MR 67/0	non-pustular	lower: 25-100% top : 10-25%
Lot 1 MR 71/0	non-pustular	lower: 25-50% top : 10-25%

FIGURE 1 - Inner surface of a DEFA round illustrating general light background of corrosion, with well defined white corrosion products plus random individual pustules of corrosion product.

x (approx.) 1

FIGURE 2 - Enlarged view of a pustule of corrosion product showing a centrally-located black mark on its upper surface.

x (approx.) 30

FIGURE 3 - Inner surface of a DEFA round showing a pattern of well defined images of propellant grains. Note the general light white corrosion product in the areas not in direct contact with the propellant grains.

x (approx.) 1



FIGURE 1



FIGURE 2

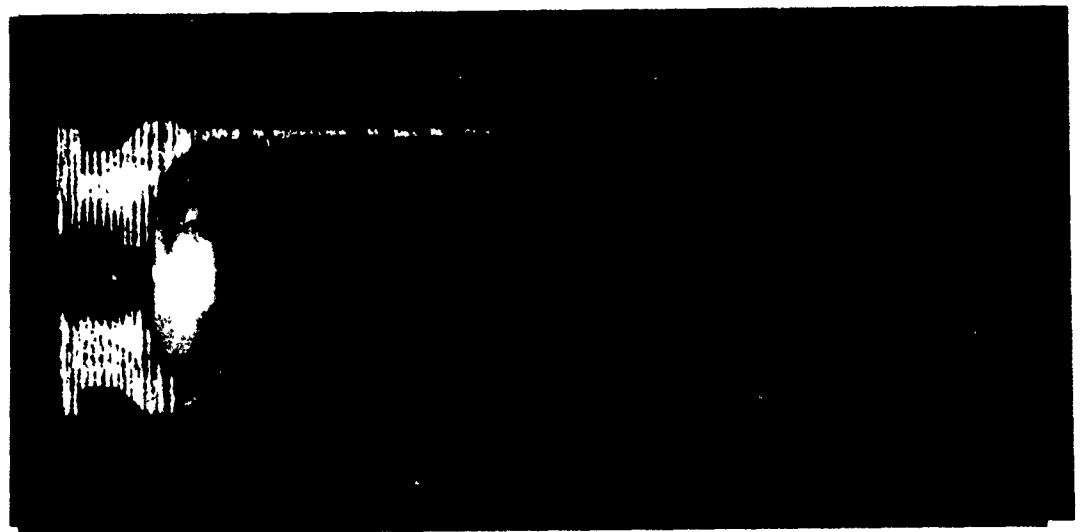
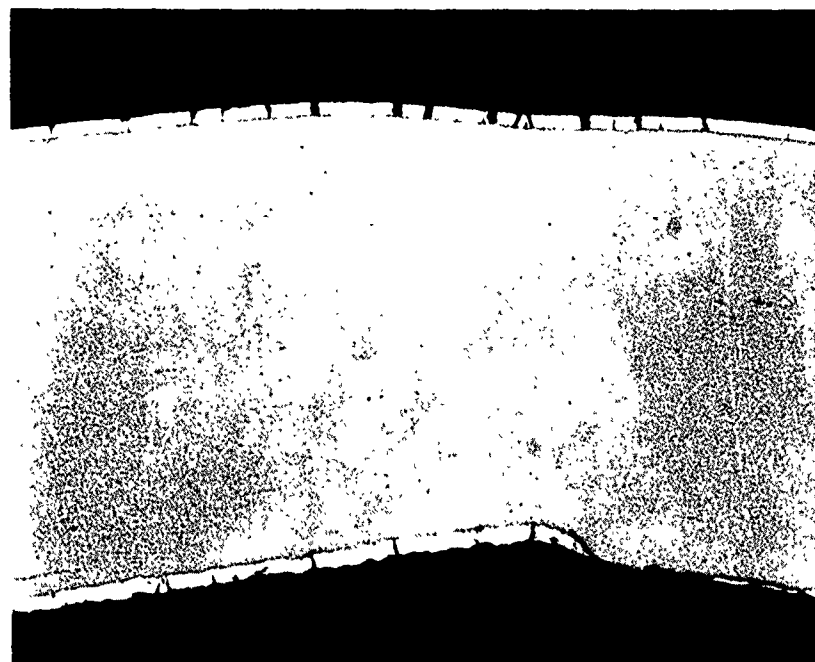


FIGURE 3



(a)



(b)

FIGURE 4 - Cross section of the DEFA case in the vicinity of the crimp area, showing cracking in the zinc electroplate. Note that the cracking does not extend into the steel substrate.

(a) x 100

(b) x 500

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